

# EXAFS in theory: an experimentalists guide to what it is and how it works

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Presented at the SSRL School on Synchrotron X-ray Absorption Spectroscopy,  
May 20, 2008

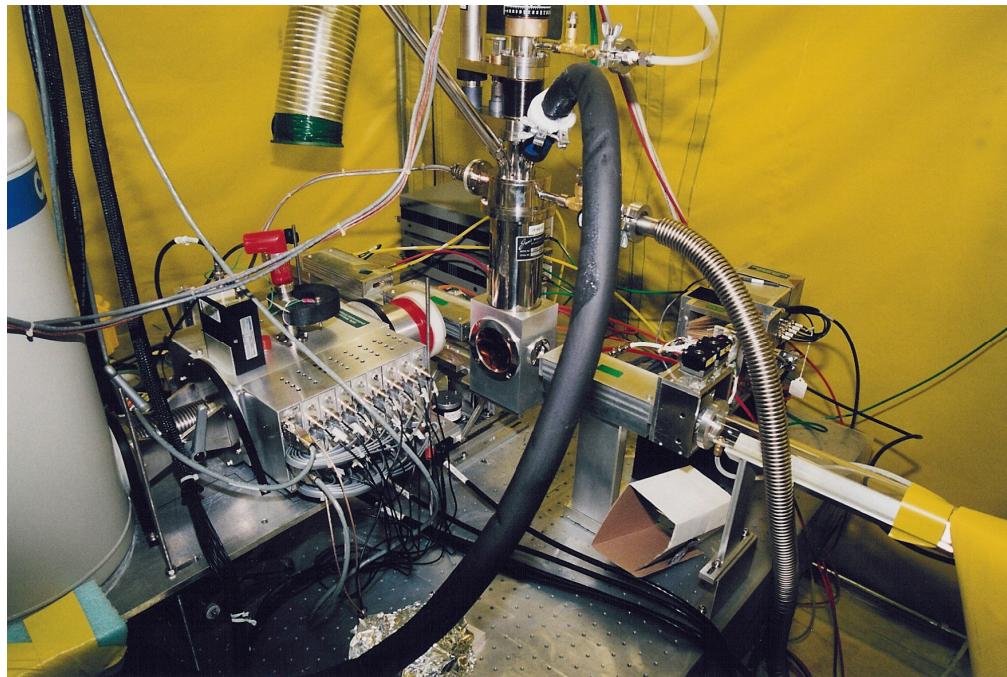
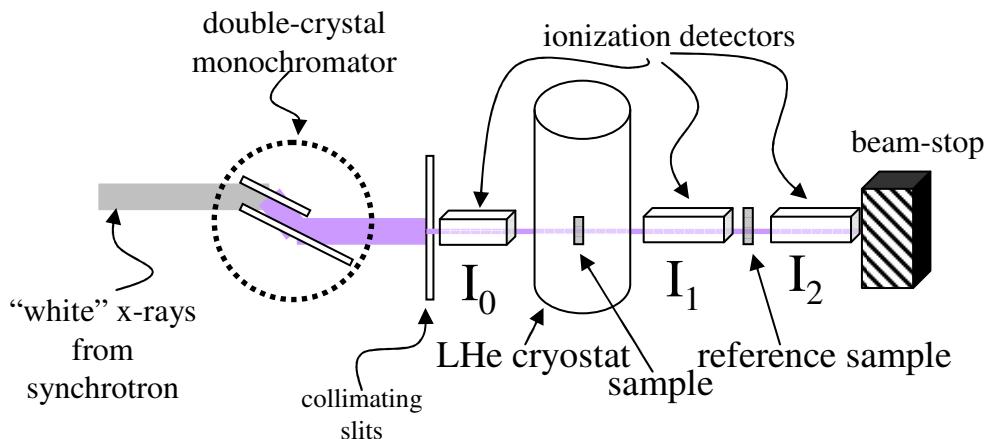
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# Topics

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1. Overview
2. Theory
  - A. Simple “heuristic” derivation
  - B. A real derivation (just for show)
  - C. polarization: oriented vs spherically averaged
3. Experiment: Corrections and Other Problems
  - A. Dead time (won’t cover)
  - B. Self-absorption
  - C. Sample issues (size effect, thickness effect, glitches) (won’t cover)
  - D. Energy resolution (won’t cover)
4. Data Analysis
  - A. Fitting procedures (Wednesday)
  - B. Fourier concepts
  - C. Systematic errors
  - D. “Random” errors
  - E. F-tests

# X-ray absorption spectroscopy (XAS) experimental setup



- sample absorption is given by

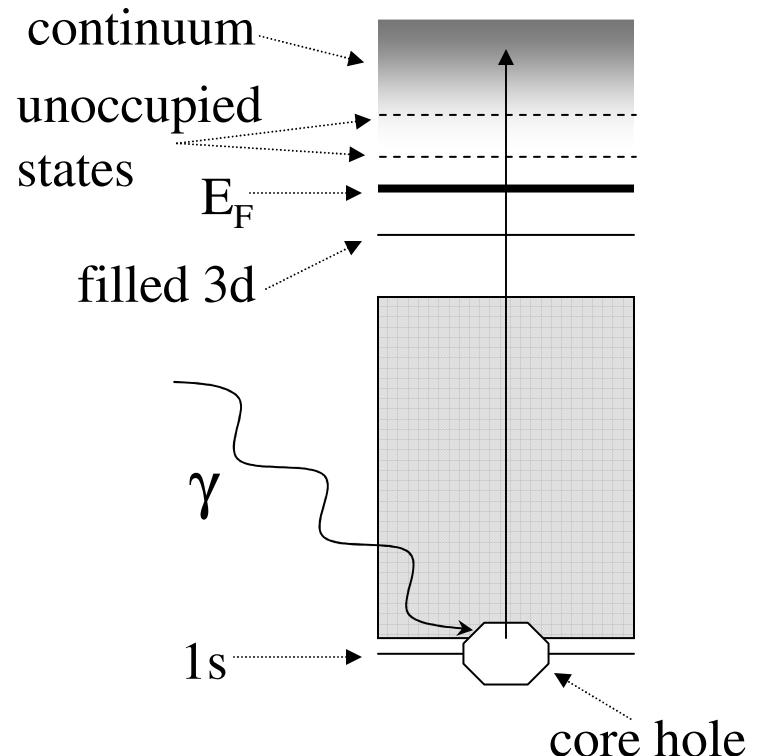
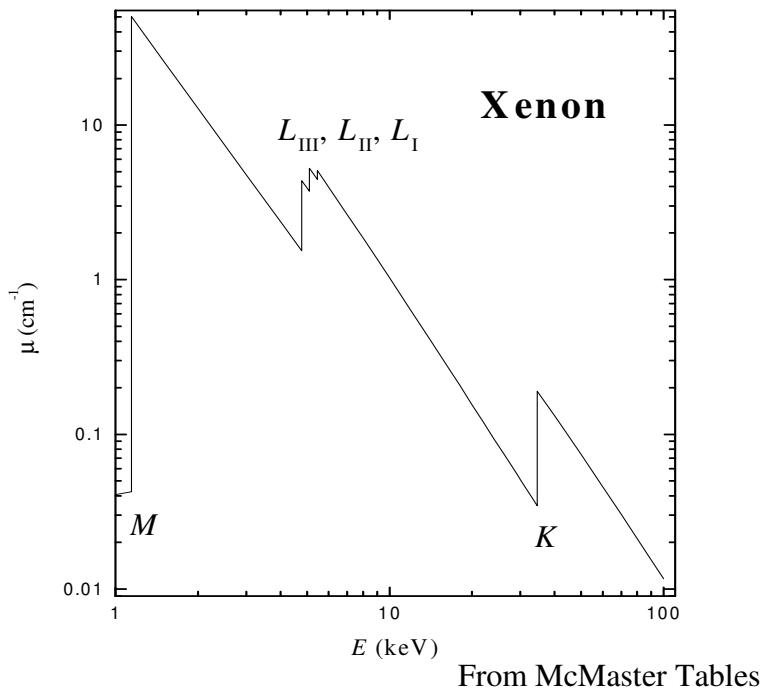
$$\mu t = \log_e(I_0/I_1)$$

- reference absorption is

$$\mu_{\text{REF}} t = \log_e(I_1/I_2)$$

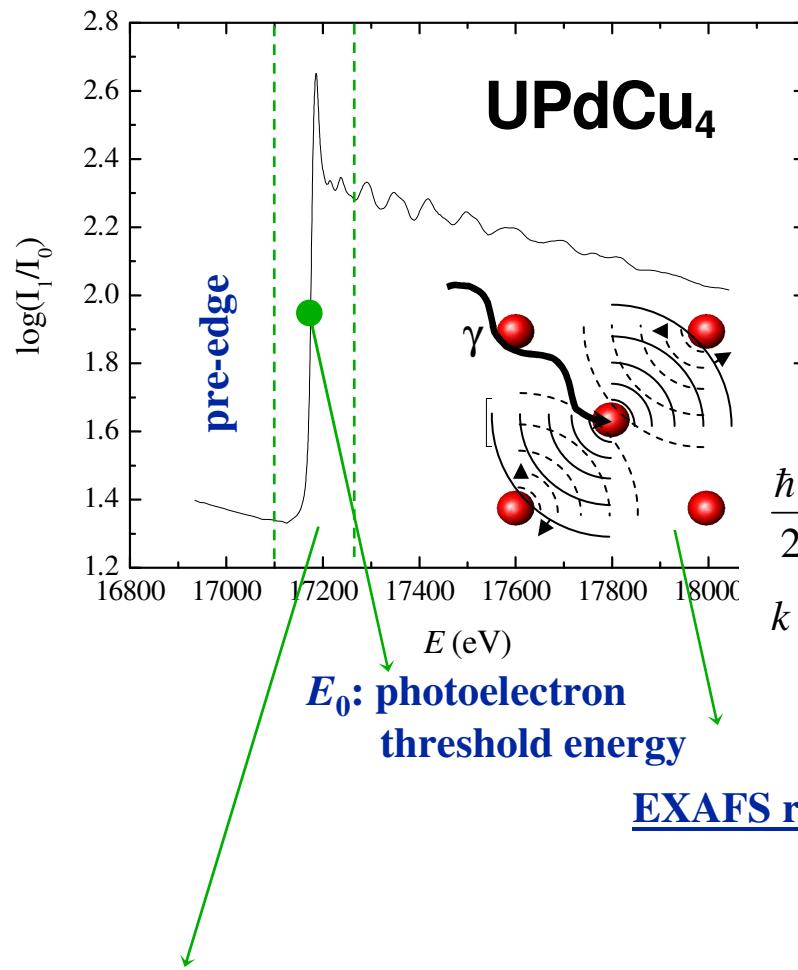
- NOTE: because we are always taking relative-change ratios, *detector gains don't matter!*

# X-ray absorption spectroscopy



- Main features are single-electron excitations.
- Away from edges, energy dependence fits a power law:  $\mu \propto AE^{-3} + BE^{-4}$  (Victoreen).
- Threshold energies  $E_0 \sim Z^2$ , absorption coefficient  $\mu \sim Z^4$ .

# X-ray absorption fine-structure (XAFS) spectroscopy

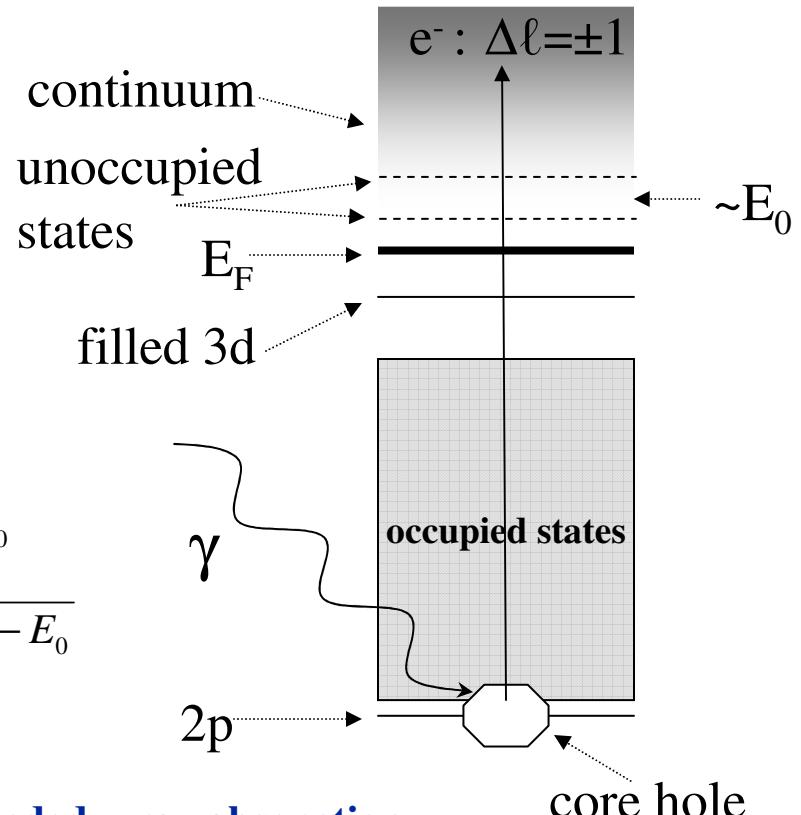


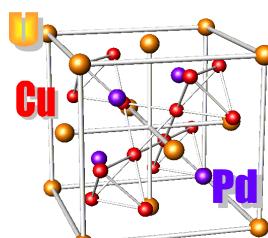
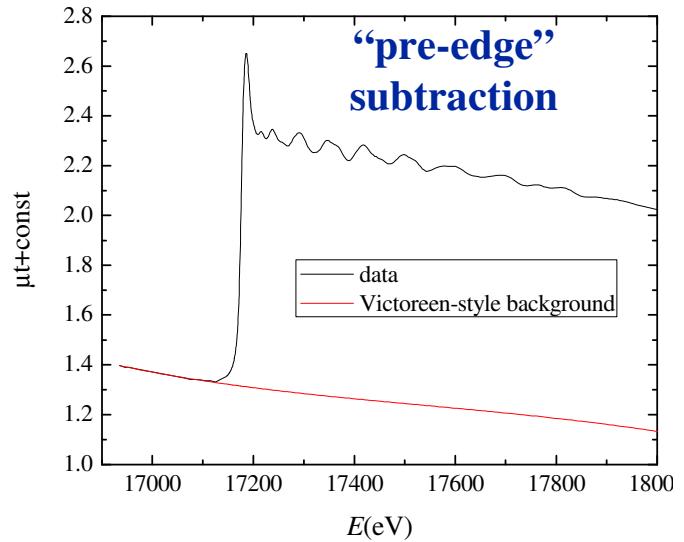
$$\frac{\hbar^2 k^2}{2m_e} = E - E_0$$

$$k = 0.512 \sqrt{E - E_0}$$

EXAFS region: extended x-ray absorption fine-structure

“edge region”: x-ray absorption near-edge structure (XANES)  
near-edge x-ray absorption fine-structure (NEXAFS)

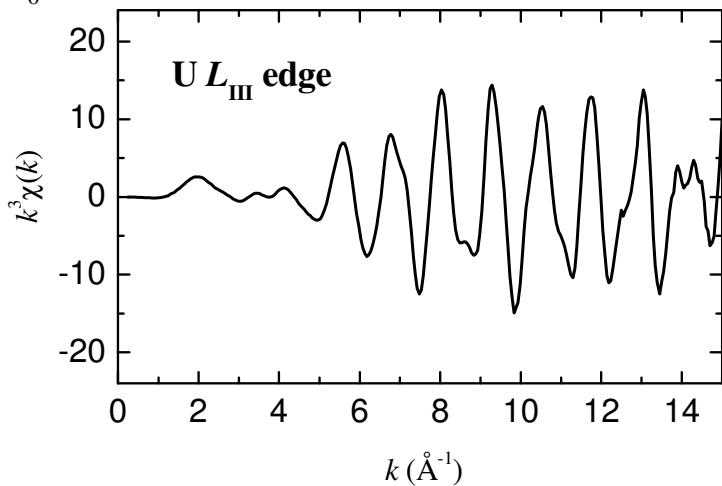
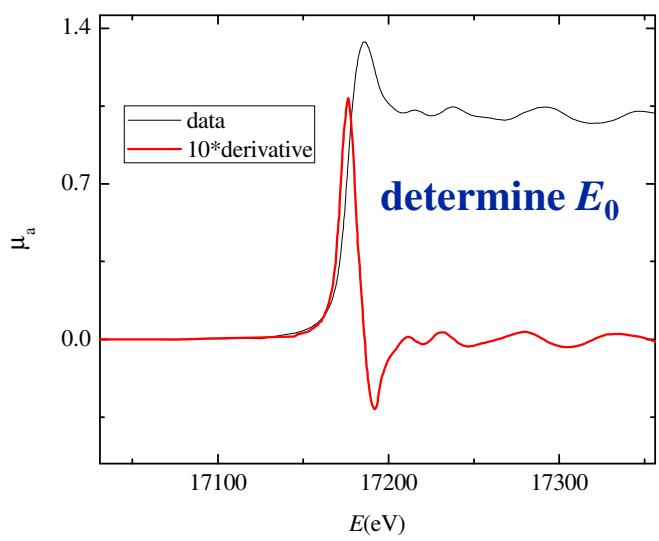
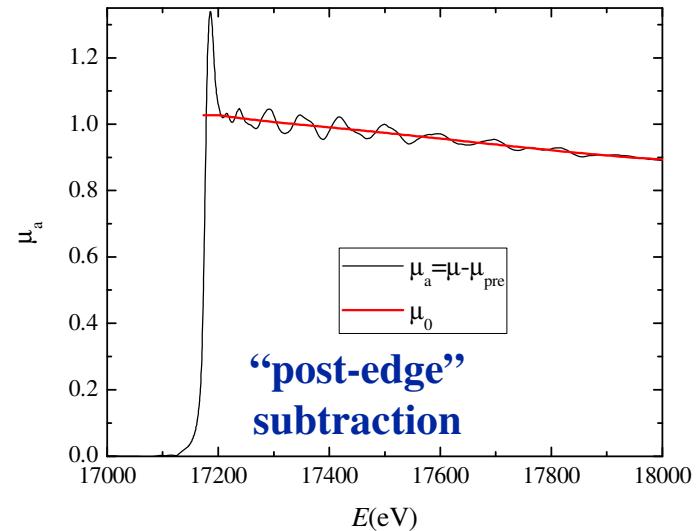




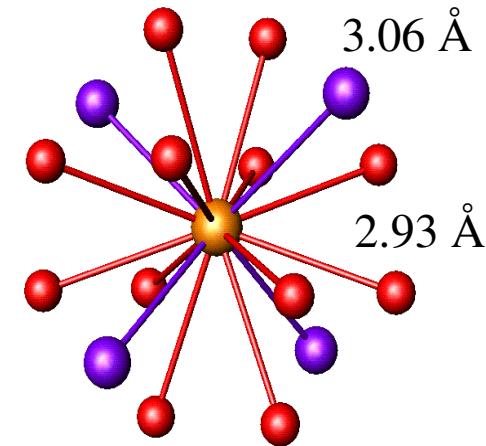
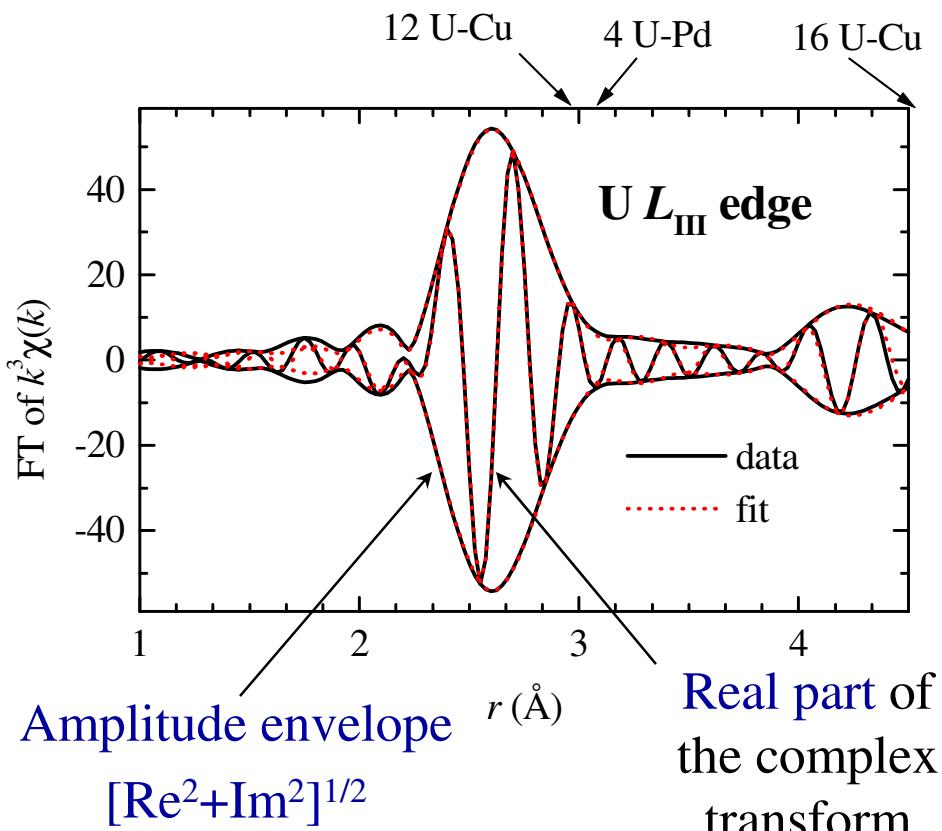
$$\chi(k) = \frac{\mu_a - \mu_0}{\mu_0}$$

$$\frac{\hbar^2 k^2}{2m_e} = E - E_0$$

$$k = 0.512 \sqrt{E - E_0}$$



# How to read an XAFS spectrum



$$\chi(k) \propto \sum_i N_i \int g(r) F(k, r) \sin(2kr + \phi_{ci}) dr$$

$g$  is a radial pair - distribution function

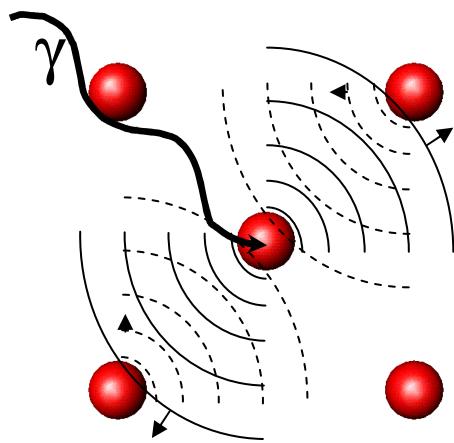
- Peak width depends on back-scattering amplitude  $F(k, r)$  , the Fourier transform (FT) range, and the distribution width of  $g(r)$ , a.k.a. the Debye-Waller s.
- Do NOT read this strictly as a radial-distribution function! Must do detailed FITS!

# “Heuristic” derivation

- In quantum mechanics, absorption is given by “Fermi’s Golden Rule”:

$$\mu \sim |\langle f | \hat{\epsilon} \cdot \hat{r} | i \rangle|^2$$

$$|f\rangle = |f_0\rangle + |\Delta f\rangle \quad \mu \sim |\langle f | \hat{\epsilon} \cdot \hat{r} | i \rangle|^2 = |\langle f_0 + \Delta f | \hat{\epsilon} \cdot \hat{r} | i \rangle|^2 \\ = |\langle f_0 | \hat{\epsilon} \cdot \hat{r} | i \rangle|^2 + \langle i | \hat{\epsilon} \cdot \hat{r} | f_0 \rangle \langle \Delta f | \hat{\epsilon} \cdot \hat{r} | i \rangle \\ + c.c. + h.o.t.$$



$$\chi = \frac{\mu - \mu_0}{\mu_0} = \frac{\Delta \mu}{\mu_0}$$

Note, this is the same as saying  
this is the change in the  
absorption *per photoelectron*

# How is final state wave function modulated?

- Assume photoelectron reaches the continuum within dipole approximation:

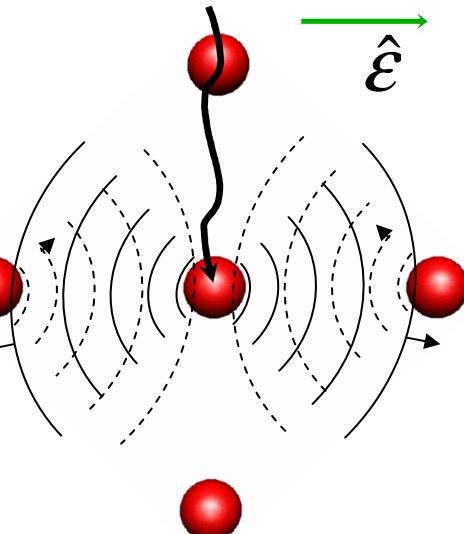
$$(\hat{\mathcal{E}} \cdot \hat{r})^2 \frac{e^{-ikr}}{kr}$$

$$(\hat{\mathcal{E}} \cdot \hat{r})^2 \frac{e^{-ikr+i\delta_c(k)}}{kr} \text{ central atom phase shift } \delta_c(k)$$

$$(\hat{\mathcal{E}} \cdot \hat{r})^2 \frac{e^{-ikR+i\delta_c(k)}}{kR} e^{-R/\lambda(k)} \text{ electronic mean-free path } \lambda(k)$$

$$(\hat{\mathcal{E}} \cdot \hat{r})^2 \frac{e^{-ikR+i\delta_c(k)}}{kR} kf(\pi, k) e^{-R/\lambda(k)} \text{ complex backscattering probability } kf(\pi, k)$$

$$(\hat{\mathcal{E}} \cdot \hat{r})^2 \frac{e^{-ikR+i\delta_c(k)}}{kR} k |f(\pi, k)| e^{-R/\lambda(k)} \frac{e^{-ik(R-r)+i\delta_c(k)+i\delta_a(k)}}{kR}$$



complex=magnitude and phase:  
backscattering atom phase shift  $\delta_a(k)$

$$\text{Im}(\hat{\mathcal{E}} \cdot \hat{r})^2 \frac{e^{-i2kR+i2\delta_c(k)+i\delta_a(k)}}{kR^2} |f(\pi, k)| e^{-2R/\lambda(k)} \text{ final interference modulation per point atom!}$$

## Other factors

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- Allow for multiple atoms  $N_i$  in a shell  $i$  and a distribution function of bondlengths within the shell  $g(r)$

$$\chi(k) = S_0^2 \sum_i N_i \int (\hat{\mathcal{E}} \cdot \hat{r})^2 |f(\pi, k)| e^{-2r/\lambda(k)} g(r) \frac{\sin 2kr + 2\delta_c(k) + \delta_a(k)}{kr^2} dr$$

where  $g(r) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(r-R_i)^2}{2\sigma^2}}$  and  $S_0^2$  is an inelastic loss factor

$$\chi(k) \approx S_0^2 \sum_i N_i (\hat{\mathcal{E}} \cdot \hat{r})^2 |f(\pi, k)| e^{-2r/\lambda(k)} e^{-2k^2\sigma^2} \frac{\sin 2kr + 2\delta_c(k) + \delta_a(k)}{kr^2}$$

Assumed plane wave scattering, curved wave has r-dependence  
solution: substitute  $F_{\text{eff}}$  full curved wave theory

Assumed both harmonic potential AND  $k\sigma \ll 1$ : problem at high  $k$  and  $\sigma$

# EXAFS equation derivation

- This “simple” version is from the Ph.D. thesis of Guoguong Li, UC Santa Cruz 1994, adapted from Teo, adapted from Lee 1974. See also, Ashley and Doniach 1975.

The probability of emitting an electron in the direction  $\hat{k}$  is given by:

$$P(\hat{k}) = D \left| \hat{\mathcal{E}} \cdot \hat{k} + \frac{f(\theta, k)}{r} e^{ikr(1-\cos\theta)} \hat{\mathcal{E}} \cdot \hat{r} + \frac{f(\pi, k) f^c(\pi - \theta, k)}{r^2} e^{2ikr} \hat{\mathcal{E}} \cdot \hat{r} \right|^2$$

The absorption is therefore:

$$\mu(k) = \frac{1}{4\pi} \int P(\hat{k}) d\hat{k} \cong \mu_0(k) + 2D \operatorname{Re}[(I_1 + I_2) \frac{\hat{\mathcal{E}} \cdot \hat{r}}{r} e^{ikr}] + DI_3 + O(\frac{1}{r^3})$$

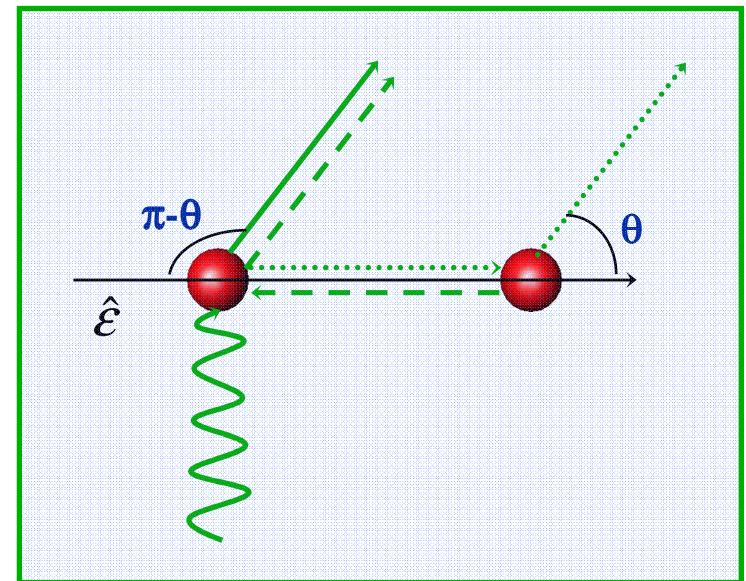
where:

$$\mu_0(k) = \frac{D}{4\pi} \int (\hat{\mathcal{E}} \cdot \hat{k})^2 d\hat{k}$$

$$I_1 = \frac{1}{4\pi} \int (\hat{\mathcal{E}} \cdot \hat{k}) e^{ikr \cos\theta} f(\theta, k) d\hat{k}$$

$$I_2 = \frac{1}{4\pi} \int (\hat{\mathcal{E}} \cdot \hat{k}) e^{ikr} f(\pi, k) \frac{f^c(\pi - \theta, k)}{r} d\hat{k}$$

$$I_3 = \frac{(\hat{\mathcal{E}} \cdot \hat{r})^2}{4\pi} \int |f(\theta, k)|^2 d\hat{k}$$



## derivation continued...

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- Some, er, “simplifications”:

$$\hat{\epsilon}(\theta', \varphi') \cdot \hat{k}(\theta, \varphi) = \frac{4\pi}{3} \sum_{m=-l}^{m=l} Y_{l,m}(\theta, \varphi) Y_{l,m}(\theta', \varphi')$$

$$e^{-ik \cos \theta} = \sum_l (2l+1)(-1)^l j_l(kr) P_l(\cos \theta)$$

$$f(\theta, k) = \sum_{l'} f_{l'}(k) P_{l'}(\cos \theta)$$

$$f_{l'}(k) = \frac{1}{2ki} (2l'+1) (e^{2i\delta_{l'}} - 1)$$

$$\int_{-1}^1 x P_l(x) P_{l'}(x) dx = \frac{1}{2l+1} \frac{2}{2l'+1} \delta_{l-1, l'} + \frac{l+1}{2l+1} \frac{2}{2l'+1} \delta_{l+1, l'}$$

$$\text{Im}[f(0, k)] = \int |f(\theta, k)|^2 d\varphi d(\cos \theta)$$

## derivation continued...

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- Rewrite  $I_1$ ,  $I_2$  and  $I_3$

$$\begin{aligned} I_1 &= \frac{\hat{\mathcal{E}} \cdot \hat{r}}{4\pi} \int_0^\pi d\varphi \int_0^{2\pi} \cos \theta e^{-ikr \cos \theta} f(\theta, k) \sin \theta d\theta \\ &= \frac{\hat{\mathcal{E}} \cdot \hat{r}}{2} \sum_l \frac{2f_l(k)}{2l+1} [(l+1)(-i)^{l+1} j_{l+1}(kr) + l(-i)^{l-1} j_{l-1}(kr)] \end{aligned}$$

and now for the key step,  $j_l(kr) \rightarrow \frac{1}{kr} \sin(kr - \frac{l\pi}{2})$  for  $kr \gg 1$

$$\begin{aligned} &= \frac{\hat{\mathcal{E}} \cdot \hat{r}}{2} \sum_l \frac{2f_l(k)}{2l+1} \frac{(-i)^{l-1}}{2kri} [-(l+1)(e^{-ikr - \frac{l+1}{2}\pi i} - e^{-ikr + \frac{l+1}{2}\pi i}) + l(e^{-ikr - \frac{l-1}{2}\pi i} - e^{-ikr + \frac{l-1}{2}\pi i})] \\ &= \frac{i\hat{\mathcal{E}} \cdot \hat{r}}{2kr} \sum_l [(-1)^l f_l(k)e^{ikr} + f_l(k)e^{-ikr}] \\ &= \frac{i\hat{\mathcal{E}} \cdot \hat{r}}{2kr} [f(\pi, k)e^{ikr} + f_l(0, k)e^{-ikr}] \end{aligned}$$

## derivation continued...

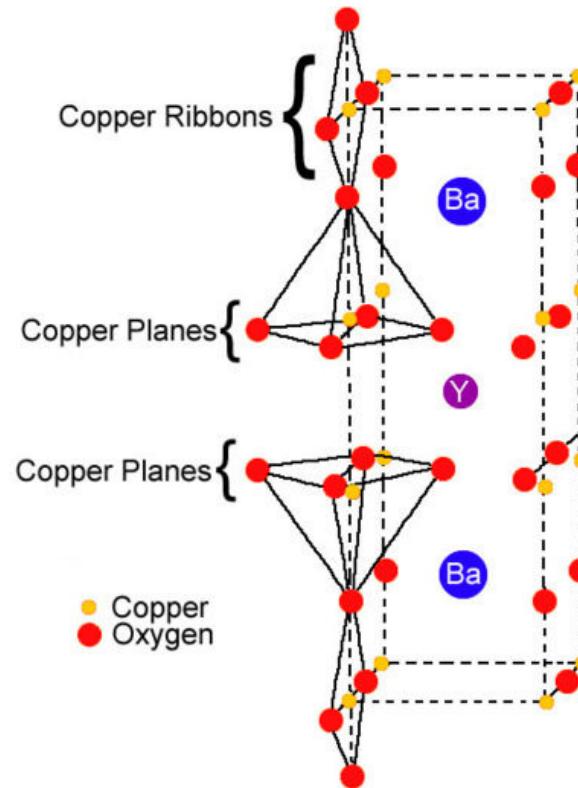
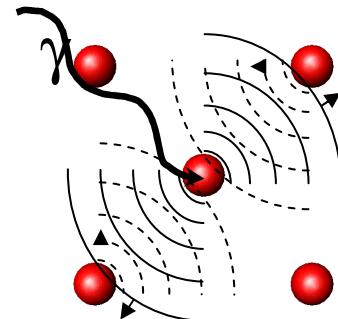
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$$\begin{aligned} I_2 &= \frac{f(\pi, k)}{2r} e^{ikr} \cos \theta \int_0^\pi \cos \theta f^c(\pi - \theta, k) \sin \theta d\theta \\ &= \frac{\hat{\mathcal{E}} \cdot \hat{r} e^{ikr} f(\pi, k)}{2r} \sum_l \frac{1}{2ki} (2l+1)(2i\delta_l^c - 1) \int_{-1}^1 x(-1)^l P_l(x) dx \\ &= \frac{i \hat{\mathcal{E}} \cdot \hat{r}}{2r} (1 - e^{2i\delta_l^c}) f(\pi, k) e^{ikr} \\ I_3 &= \frac{(\hat{\mathcal{E}} \cdot \hat{r})^2}{kr^2} \operatorname{Im} f(0, k) \end{aligned}$$

# Finishing derivation, beginning polarization

$$\mu(k) = \frac{D}{3} - \frac{D(\hat{\mathcal{E}} \cdot \hat{r})^2}{kr^2} \operatorname{Im}[e^{2ikr+2i\delta_l^c} f(\pi, k)]$$

$$\begin{aligned}\chi(k) &= \frac{\mu - \mu_0}{\mu_0} \\ &= \frac{3(\hat{\mathcal{E}} \cdot \hat{r})^2}{kr^2} \operatorname{Im}[e^{2ikr+2i\delta_l^c} f(\pi, k)] \\ &= \frac{3\cos^2 \theta}{kr^2} f(\pi, k) \sin[2ikr + 2i\delta_l^c + \phi(k)] \quad \text{for a K-edge}\end{aligned}$$



- Notice  $\theta$  (angle w.r.t. polarization): can eliminate certain peaks!

## L<sub>2</sub> and L<sub>3</sub> edges appear more complicated

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- 2p<sub>1/2</sub> or 2p<sub>3/2</sub> core hole and a mixed s and d final state

$$\chi(k) = \frac{1}{|\langle 2|1\rangle|^2 + \frac{1}{2}|\langle 0|1\rangle|^2} \frac{|f(\pi, k)|}{kr^2} \{ \langle 1|2\rangle\langle 0|1\rangle \sin[2kr + \delta_{02}(k)](1 - 3\cos^2\theta) \\ + \frac{|\langle 2|1\rangle|^2}{2} \sin[2kr + \delta_2(k)](1 + 3\cos^2\theta) \\ + \frac{|\langle 0|1\rangle|^2}{2} \sin[2kr + \delta_0(k)] \}$$

Heald and Stern 1977

# polarization vs. spherically averaged

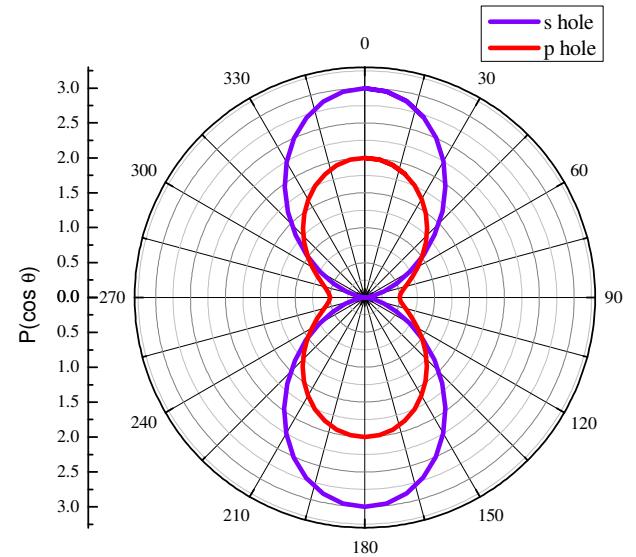
- L<sub>2</sub> and L<sub>3</sub> mostly d final states (yeah!)

$$\frac{\langle 2|1\rangle}{\langle 0|1\rangle} \approx 5$$

$$(1+3\langle \cos^2 \theta \rangle) \frac{|\langle 2|1\rangle|^2}{|\langle 0|1\rangle|^2} \approx 50$$

$$\chi(k) = -P(\cos \theta) \frac{|f(\pi, k)|}{kr^2} \sin[2kr + \phi(k)]$$

$$P(\cos \theta) = \begin{cases} 3\cos^2 \theta & \text{for K and L}_1 \text{ edges} \\ -\frac{1}{2}(1+3\cos^2 \theta) & \text{for L}_{\text{II}} \text{ and L}_{\text{III}} \text{ edges} \end{cases}$$



Stern 1974

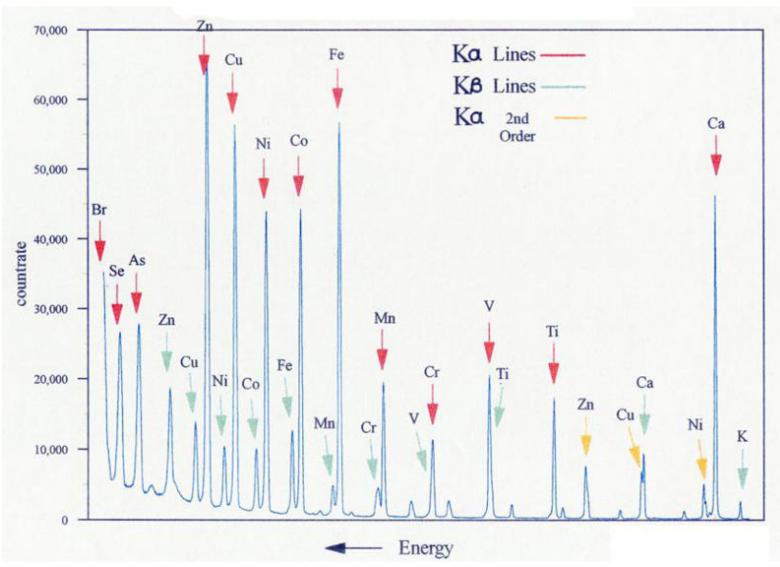
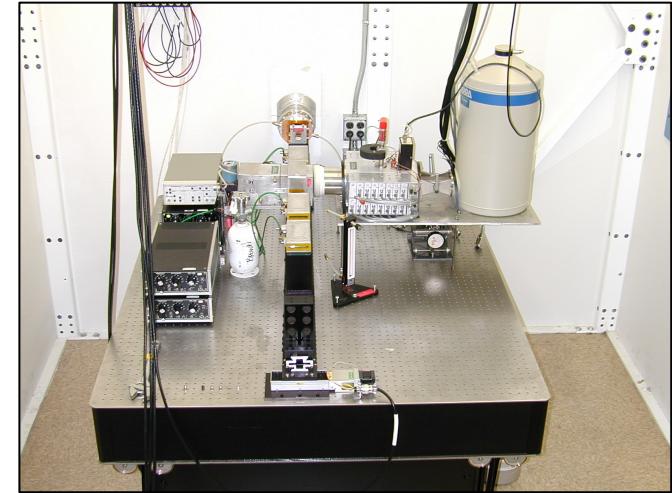
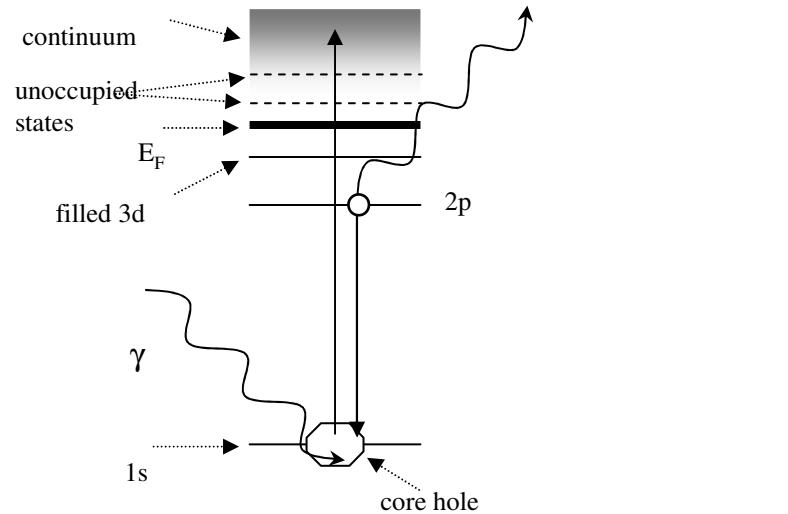
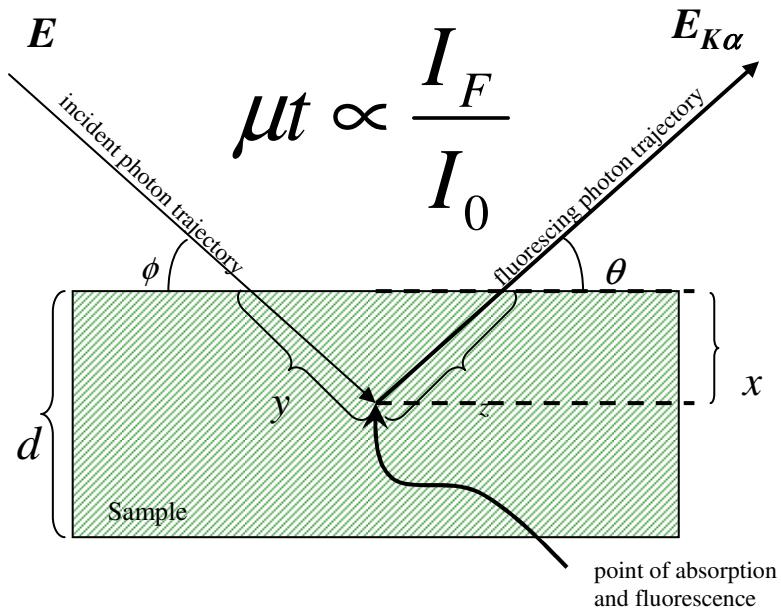
Heald and Stern 1977

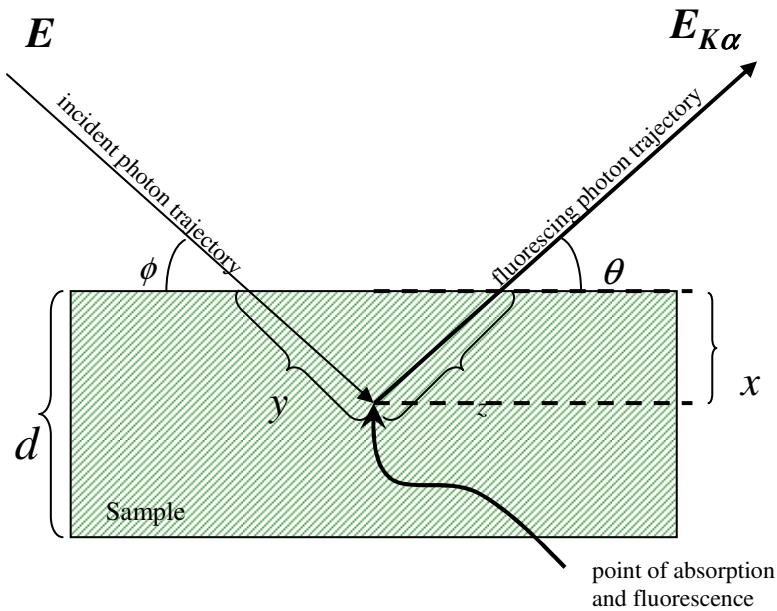
# Corrections and Concerns

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- “Normal” EXAFS performed on powder samples in transmission
  - can tune the thickness
    - Want  $\Delta\mu t \sim < 1$  and  $\mu t < 3$
    - We like stacking strips of scotch tape
  - can make a flat sample
  - diffraction off the sample not a problem
- Working with oriented materials: single crystals, films
  - usually *cannot* get the perfect thickness: too thick
    - fluorescence mode data collection
    - self-absorption can be substantial!
    - dead-time of the detector

# Fluorescence mode

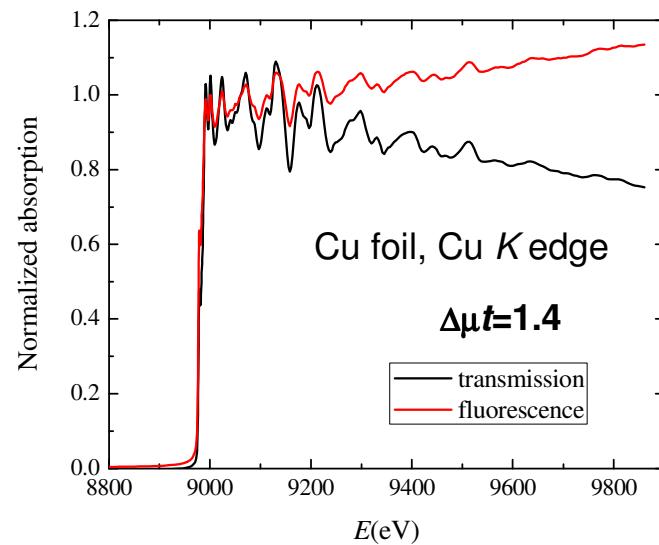




$$\chi_{\text{exp}} = \frac{I_F}{I_0} - 1$$

L. Tröger , D. Arvanitis, K. Baberschke, H. Michaelis, U. Grimm, and E. Zschech, Phys. Rev. B **46**, 3283 (1992).

- Fluorescing photon can be absorbed on the way out
- Competing effects:
  - glancing angle, sample acts very thick, always get a photon, XAFS damped
  - normal-incidence: escaping photon depth fixed



# The full correction

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- With the above approximation, we can finally write the full correction:

$$\chi = \frac{1}{2\beta} \left\{ -[\gamma(\alpha - \bar{\mu}_a(\chi_{\text{exp}} + 1)) + \beta] + \sqrt{[\gamma - \bar{\mu}_a(\chi_{\text{exp}} + 1)) + \beta]^2 + 4\alpha\beta\gamma\chi_{\text{exp}}} \right\}$$

- In the thick limit ( $d \rightarrow \infty$ ), this treatment gives:

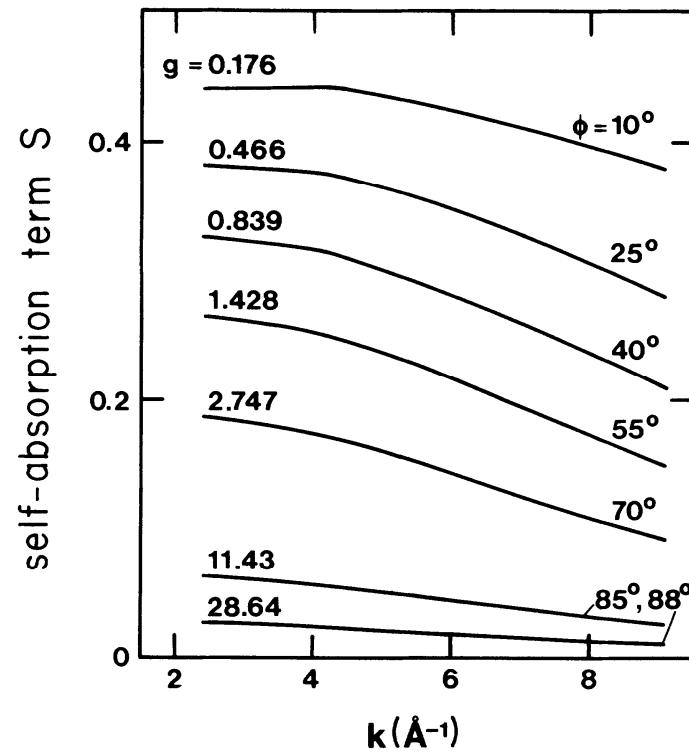
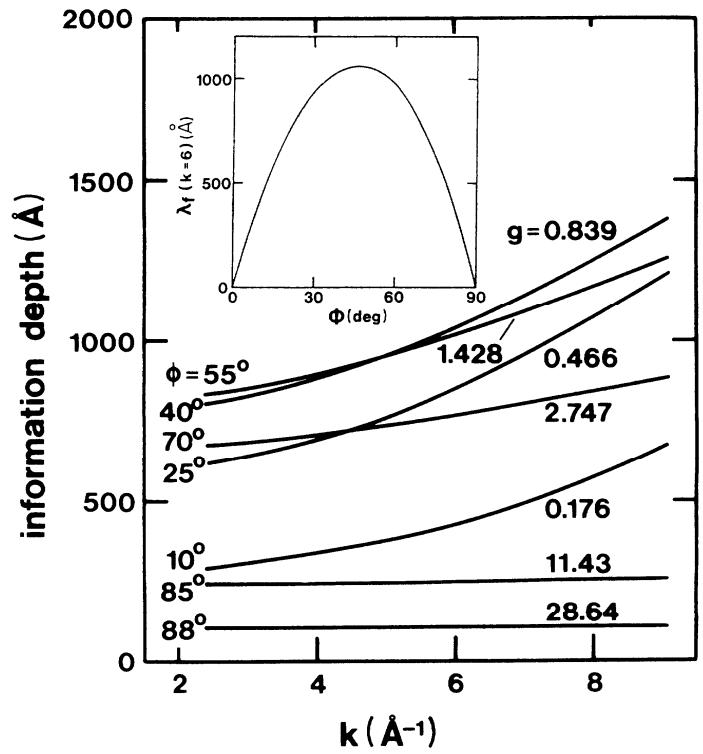
$$\chi = \frac{\chi_{\text{exp}}}{1 - \frac{\bar{\mu}_a}{\alpha} \chi_{\text{exp}} - \frac{\bar{\mu}_a}{\alpha}}$$

where

$$\alpha = \bar{\mu}_T + \frac{\sin \phi}{\sin \theta} \mu_F$$

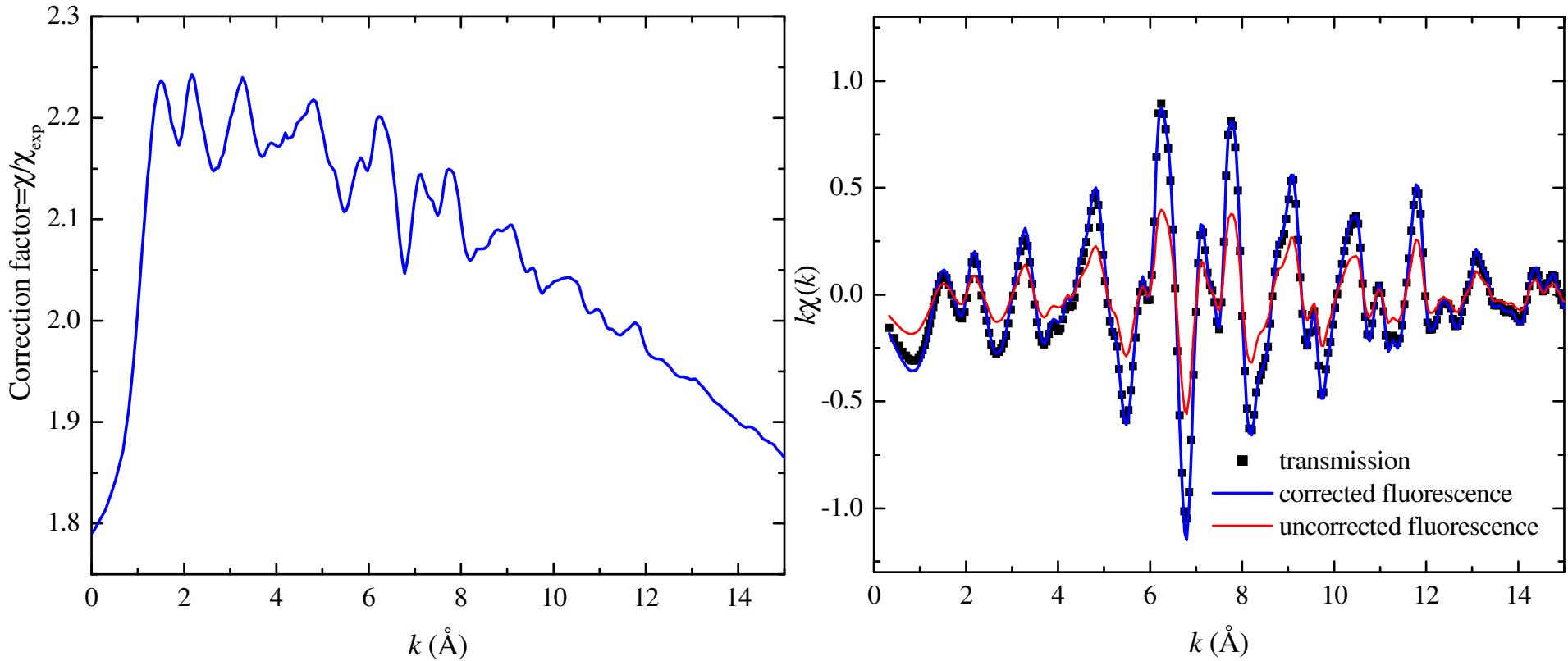
$$\beta = \frac{\bar{\mu}_a d \alpha}{\sin \phi} e^{-\frac{\alpha d}{\sin \phi}}$$

$$\gamma = 1 - e^{-\frac{\alpha d}{\sin \phi}}$$



L. Tröger , D. Arvanitis, K.  
 Baberschke, H. Michaelis, U.  
 Grimm, and E. Zschech, Phys.  
 Rev. B **46**, 3283 (1992).

# Correction applied to a 4.6 $\mu\text{m}$ Cu foil



- Data collected on BL 11-2 at SSRL in transmission and fluorescence using a 32-element Canberra germanium detector, corrected for dead time.

# Fitting the data to extract structural information

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- Fit is to the standard EXAFS equation using either a theoretical calculation or an experimental measurement of  $F_{\text{eff}}$

$$\chi(k) = S_0^2 \sum_i N_i \int (\hat{\varepsilon} \cdot \hat{r}_i)^2 |f_i(\pi, k)| e^{-2r/\lambda(k)} g_i(r) \frac{\sin 2kr + 2\delta_c(k) + \delta_i(k)}{kr^2} dr$$

- Typically, polarization is spherically averaged, doesn't have to be
- Typical fit parameters include:  $R_i$ ,  $N_i$ ,  $\sigma_i$ ,  $\Delta E_0$
- Many codes are available for performing this fits:
  - EXAFSPAK
  - IFEFFIT
    - SIXPACK
    - ATHENA
  - GNXAS
  - RSXAP

# FEFF: a curved-wave, multiple scattering EXAFS and XANES calculator

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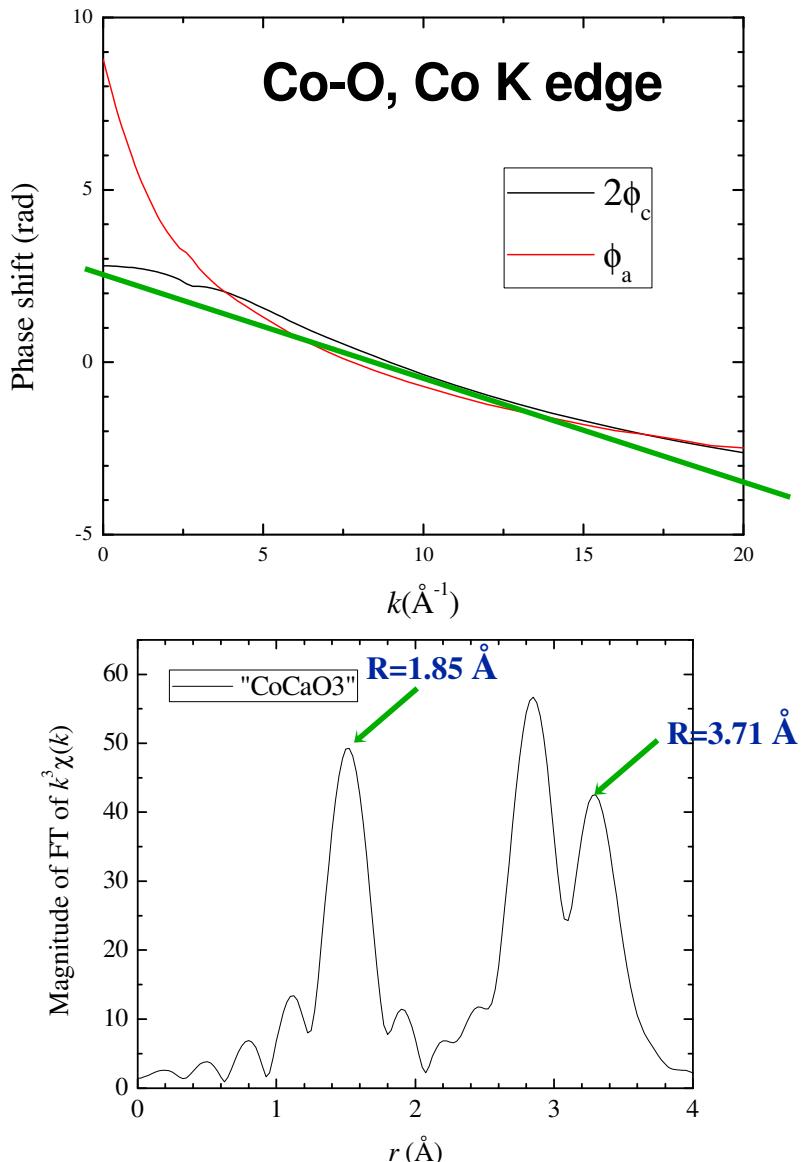
- The FEFF Project is lead by John Rehr and is very widely used and trusted
- Calculates the complex scattering function  $F_{\text{eff}}(k)$  and the mean-free path  $\lambda$

```
TITLE      CaMnO3 from Poeppelmeier 1982

HOLE 1    1.0      Mn K edge ( 6.540 keV), s0^2=1.0
POTENTIALS
*   ipot   z   label
    0     22   Mn
    1     8    O
    2    20   Ca
    3    22   Mn

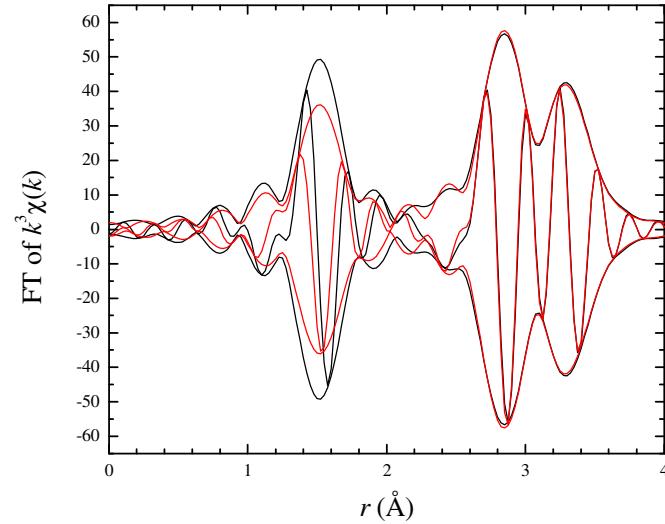
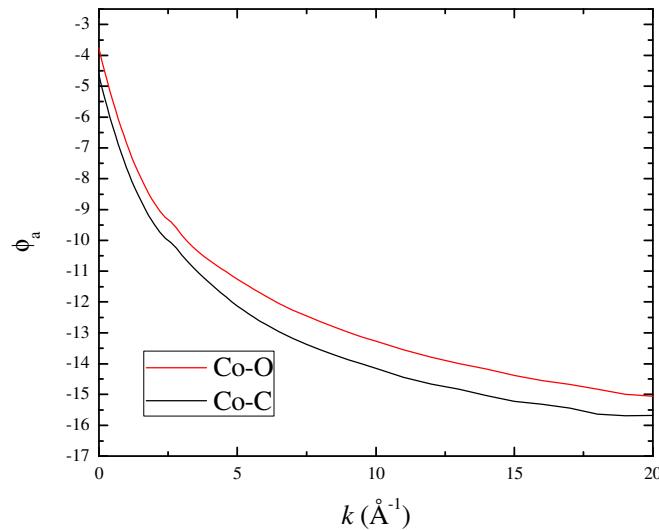
ATOMS
  0.00000   0.00000   0.00000   0   Mn   0.00000
  0.00000  -1.85615   0.00000   1   O(1)  1.85615
  0.00000   1.85615   0.00000   1   O(1)  1.85615
 -1.31250   0.00000   1.31250   1   O(2)  1.85616
  1.31250   0.00000  -1.31250   1   O(2)  1.85616
  1.31250   0.00000   1.31250   1   O(2)  1.85616
 -1.31250   0.00000  -1.31250   1   O(2)  1.85616
  0.00000   1.85615  -2.62500   2   Ca   3.21495
 -2.62500   1.85615   0.00000   2   Ca   3.21495
 -2.62500  -1.85615   0.00000   2   Ca   3.21495
  0.00000   1.85615   2.62500   2   Ca   3.21495
```

# Phase shifts: functions of $k$

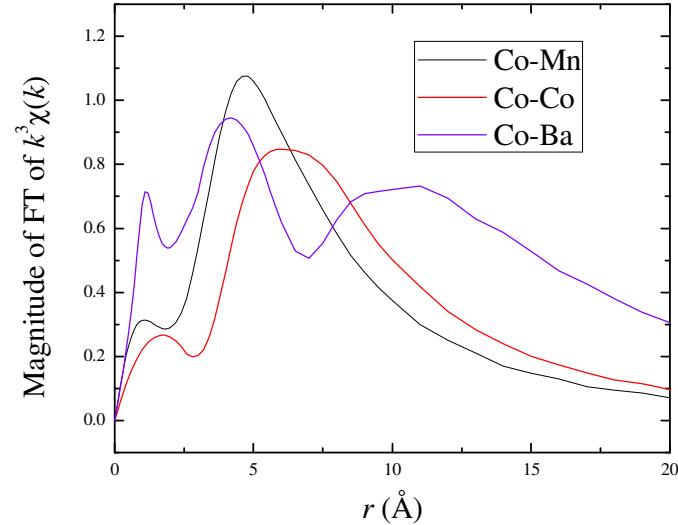


- $\sin(2kr + \phi_{\text{tot}}(k))$ : linear part of  $\phi(k)$  will look like a shift in  $r$  slope is about  $-2 \times 0.35 \text{ rad \AA}$ , so *peak in r will be shifted by about 0.35 \AA*
- Both central atom and backscattering atom phase shifts are important
- Can cause **CONFUSION**: *sometimes possible to fit the wrong atomic species at the wrong distance!*
- Luckily, different species have reasonably unique phase and scattering functions (next slide)

# Species identification: phase and magnitude signatures



- First example: same structure, first neighbor different, distance between  $\text{Re}$  and  $\text{Amp}_{\max}$  shifts
- Note Ca (peak at  $2.8 \text{\AA}$ ) and C have nearly the same profile
- Magnitude signatures then take over
- Rule of thumb is you can tell difference in species within  $\Delta Z \sim 2$ , but maintain constant vigilance!



## More phase stuff: $r$ and $E_0$ are correlated

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- When fitting,  $\Delta E_0$  generally is allowed to float (vary)
- In theory, a single  $\Delta E_0$  is needed for a monovalent absorbing species
- Errors in  $\Delta E_0$  act like a **phase shift** and correlate to errors in  $R$ !

consider error  $\epsilon$  in  $E_0$ :  $k_{\text{true}} = 0.512[E - (E_0 + \epsilon)]^{1/2}$

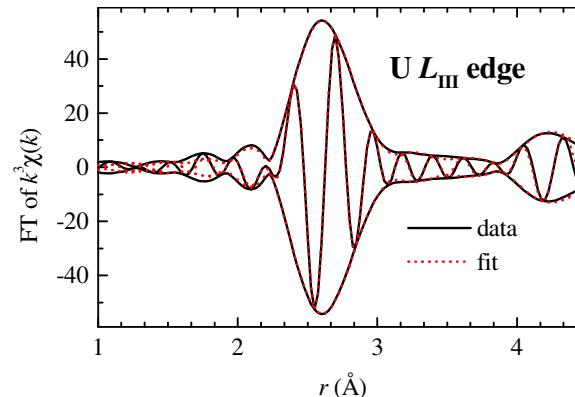
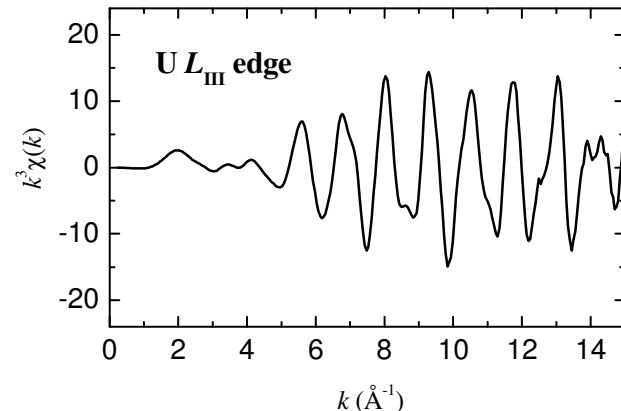
for small  $\epsilon$ ,  $k = k_0 - [(0.512)^2 / (2k_0)]\epsilon$

e.g. at  $k = 10 \text{ \AA}^{-1}$  and  $\epsilon = 1 \text{ eV}$ ,  $\Delta r \sim 0.013 \text{ \AA}$

- This correlation is not a problem if  $k_{\text{max}}$  is reasonably large
- Correlation between  $N$ ,  $S_0^2$  and  $\sigma$  is a much bigger problem!

# Information content in EXAFS

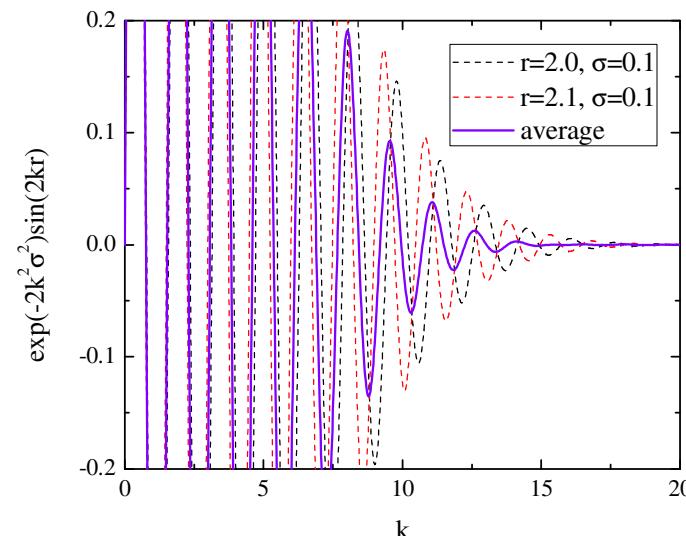
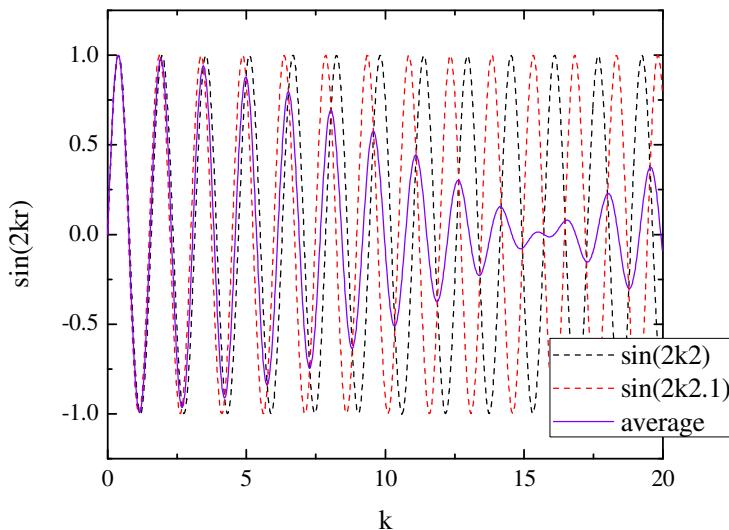
- k-space vs. r-space fitting are *equivalent* if done correctly!



- r-range in k-space fits is determined by scattering shell with highest R
- k-space direct comparisons with raw data (i.e. residual calculations) are incorrect: must Fourier filter data over r-range
- All knowledge from spectral theory applies! Especially, discrete sampling Fourier theory...

# Fourier concepts

- highest “frequency”  $r_{\max} = \pi(2\delta_k)^{-1}$  (Nyquist frequency)  
eg. for sampling interval  $\Delta k = 0.05 \text{ \AA}^{-1}$ ,  $r_{\max} = 31 \text{ \AA}$
- for  $N_{\text{data}}$ , discrete Fourier transform has  $N_{\text{data}}$ , too! Therefore...  
FT resolution is  $\delta_R = r_{\max}/N_{\text{data}} = \pi/(2k_{\max})$ , eg.  $k_{\max} = 15 \text{ \AA}^{-1}$ ,  $\delta_R = 0.1 \text{ \AA}$
- This is the ultimate limit, corresponds to when a beat is observed in two sine wave  $\delta_R$  apart. IF YOU DON’T SEE A BEAT, DON’T RELY ON THIS EQUATION!!



# More Fourier concepts

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- Assuming  $N_{\text{data}}$  are independent data points, and a fit range over  $k$  (and  $r$ ):

$$\Delta_r = r_2 - r_1 \quad \Delta_k = k_2 - k_1$$

$$r_{\max} = \frac{\pi}{2\delta_k} \quad N_{\text{data}} = \frac{k_{\max}}{\delta_k} = \frac{r_{\max}}{\delta_r}$$

$$N_{\text{ind}} = N_{\text{data}} \frac{\Delta_r}{r_{\max}} \frac{\Delta_k}{k_{\max}} = \frac{2}{\pi} \Delta_r \Delta_k \text{ Fourier result}$$

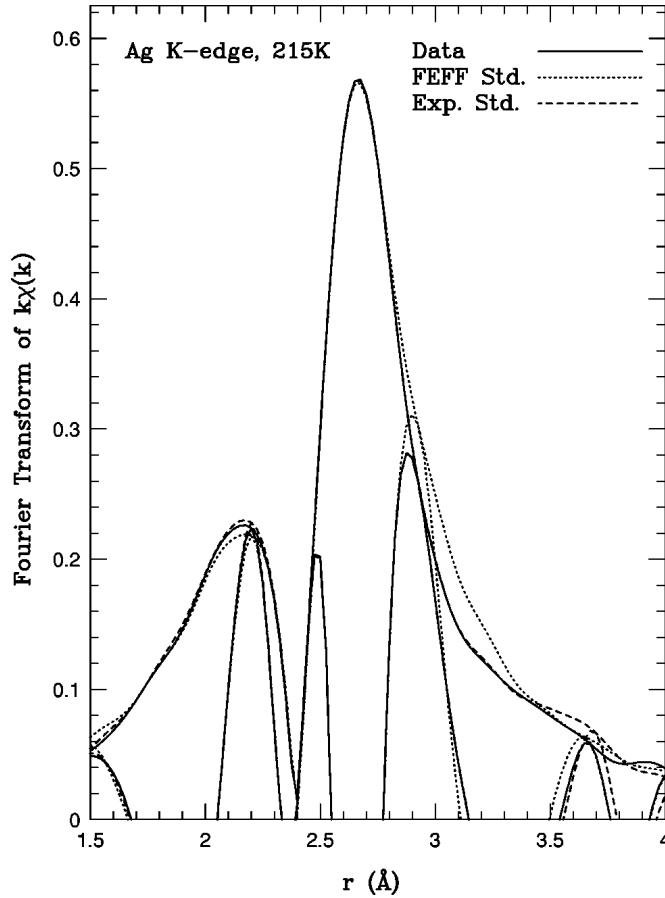
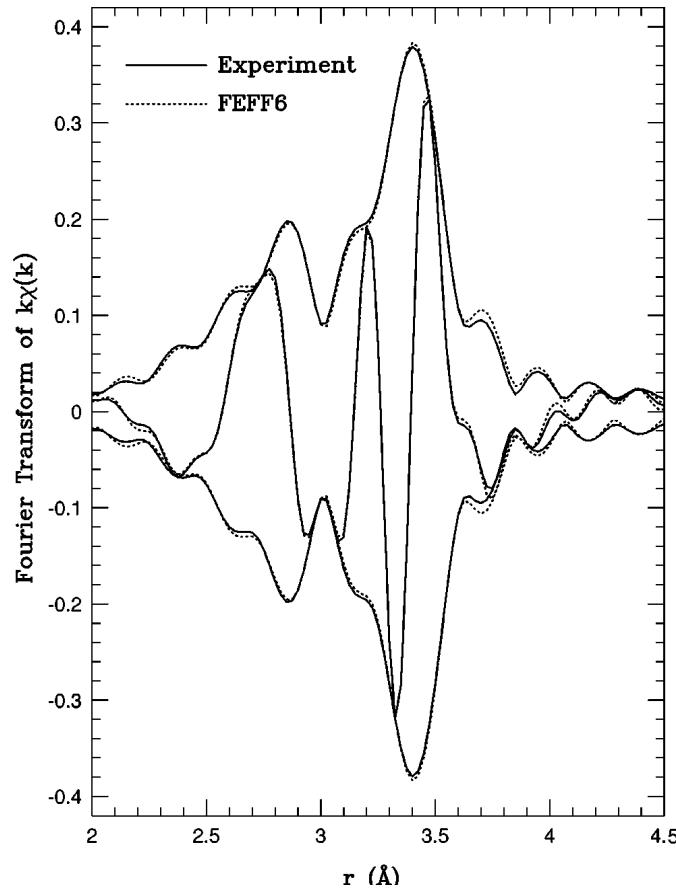
$$N_{\text{ind}} = \frac{2}{\pi} \Delta_r \Delta_k + 2 \text{ "Stern's rule" EXAFS result}$$

- Fit degrees of freedom  $v = N_{\text{ind}} - N_{\text{fit}}$
- Generally should never have  $N_{\text{fit}} >= N_{\text{ind}}$  ( $v < 1$ )
- But what does this mean? It means that

For every fit parameter exceeding  $N_{\text{ind}}$ , there is another linear combination of the same  $N_{\text{fit}}$  parameters that produces EXACTLY the same fit function

# Systematic errors: calculations *are not perfect!*

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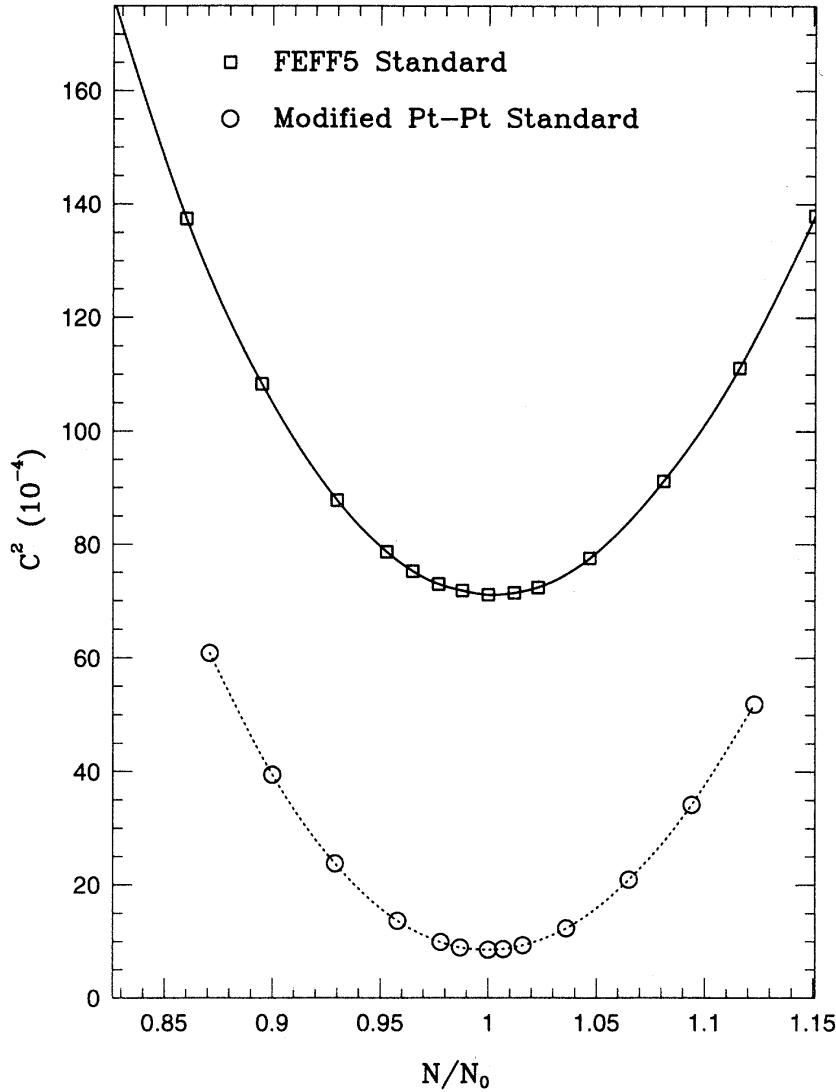
Kvitky, Bridges and van  
Dorssen, Phys. Rev. B **64**,  
214108 (2001).

# Systematic vs. Random error

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- Systematic errors for nearest-neighbor shells are about **0.005 Å in R, 5% in N, 10% in σ** (Li, Bridges, Booth 1995)
- Systematic error sources:
  - sample problems (pin holes, glitches, etc.)
  - correction errors: self-absorption, dead time, etc.
  - backscattering amplitudes
  - overfitting (too many peaks, strong correlations between parameters)
- Random error sources:
  - some sample problems (roughly, small sample and moving beam)
  - low counts (dilute samples)

# Systematic vs. Random error



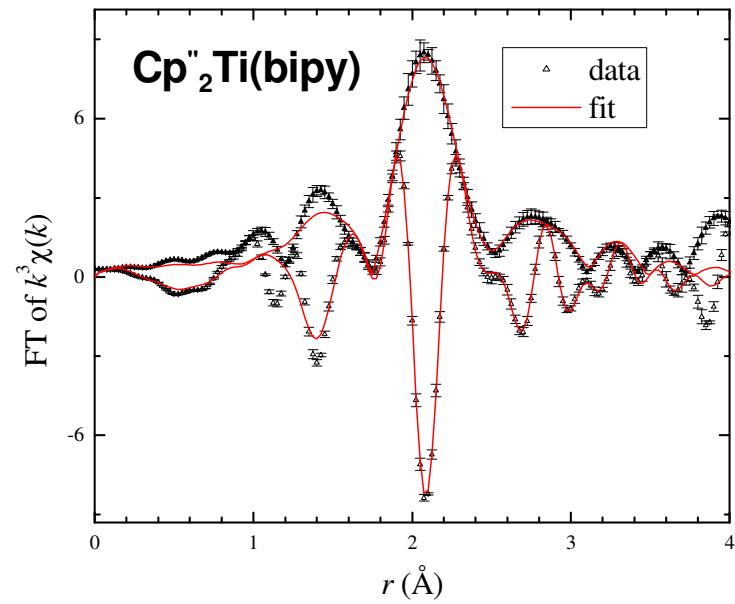
## Statistics:

$$\chi^2 = \sum_{i=1}^N \frac{(d_i - \bar{d}_i)^2}{\varepsilon_i^2}$$

$\approx v$  (degrees of freedom)

$$\chi_{\text{meas}}^2 = \chi_{\text{true}}^2 + \chi_{\text{syst}}^2$$

$\approx v + \text{constant}$



# Error analysis options

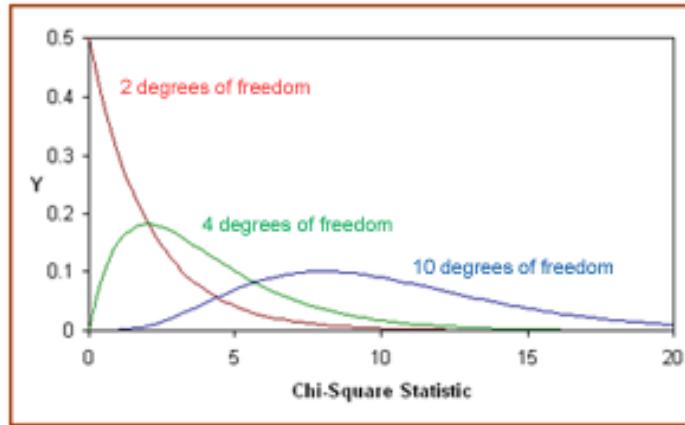
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- Use error analysis in fitting code (generally from the covariance matrix)
  - Always requires assumptions
    - a single error at all r or k is assumed
    - systematic errors ignored
    - can be useful in conjunction with other methods
- Collect several scans, make individual fits to each scan, calculate standard deviation in parameters  $p_i$ 
  - Fewer assumptions
    - random errors treated correctly as long as no nearby minima in  $\chi^2(p_i)$  exist
    - systematic errors lumped into an unaccounted shift in  $\langle p_i \rangle$
- Best method(?): Monte Carlo

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- EXAFS as a technique is not count-rate limited: It is limited by the accuracy of the backscattering functions
  - This does NOT mean that you should ignore the quality of the fit!
  - DO a Chi2 test, observe whether Chi2=degrees of freedom
    - one limit: random noise is large, and you have a statistically sound fit
    - other limit: random noise is small, and you will then know how large the problem with the fit is

# not so Advanced Topic: F-test

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- F-test, commonly used in crystallography to test one fitting model versus another

$$F = (\chi_1^2/v_1)/(\chi_0^2/v_0) \approx v_0/v_1 \times R_1^2/R_0^2$$

*(if errors approximately cancel)*

alternatively:  $F = [(R_1^2 - R_0^2)/(v_1 - v_0)] / (R_0^2/v_0)$

- Like  $\chi^2$ , F-function is tabulated, is given by incomplete beta function
- Advantages of a  $\chi^2$ -type test:
  - don't need to know the errors!

## F-test how-to

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$$R^2 = \sum_{i=1}^N (d_i - \bar{d}_i)^2 \quad \text{proper definition of a residual}$$

$$F = \frac{(R_1^2 - R_0^2)/b}{R_0^2/(n-m)} = [\mathfrak{R}^2 - 1] \frac{(n-m)}{b}$$

with  $\mathfrak{R} = \frac{R^1}{R_0}$ ,  $n$  independent data points,  $m$  fit parameters

$$\alpha = P(F > F_{b,n-m,\alpha}) = 1 - I_{\mathfrak{R}^2} \left[ \frac{n-m}{2}, \frac{b}{2} \right]$$

where  $\alpha$  is the confidence level and  $I_x[y,z]$  is an incomplete beta function

## Example and limitations

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- consider 4 different samples with various amount of species TcS<sub>x</sub>: Are they interconnected?
  - $\Delta_r = 4.5\text{-}1 \text{ \AA}$      $\Delta_k = 13.3\text{-}2 \text{ \AA}^{-1}$ ,  $n = 26.8$
  - model 0 has Tc neighbors and  $m = 14$  parameters,  $R_0 = 0.078$  to **0.096**
  - model 1 has only S neighbors and  $m = 10$ ,  $R_0 = 0.088$  to **0.11**
  - dimension of the hypothesis  $b = 14 - 10 = 4$
  - each data set,  $\alpha$  between 35 and 82%, all together **99.9%**
- Effect of systematic error: increases  $R_0$  and  $R_1$  same amount
- This will decrease the % improvement, making it harder to pass the F-test (right direction!)
- Failure mode: fitting a peak due to systematic errors in  $F_{\text{eff}}$

# Finishing up

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- **Never report two bond lengths that break the rule**
- **Break Stern's rule only with extreme caution**
- **Pay attention to the statistics**

# Further reading

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- Overviews:
  - B. K. Teo, “EXAFS: Basic Principles and Data Analysis” (Springer, New York, 1986).
  - Hayes and Boyce, *Solid State Physics* 37, 173 (192).
- Historically important:
  - Sayers, Stern, Lytle, *Phys. Rev. Lett.* 71, 1204 (1971).
- History
  - Lytle, *J. Synch. Rad.* 6, 123 (1999).  
(<http://www.exafscopy.com/techpapers/index.html>)
  - Stumm von Bordwehr, *Ann. Phys. Fr.* 14, 377 (1989).
- Theory papers of note:
  - Lee, *Phys. Rev. B* 13, 5261 (1976).
  - Rehr and Albers, *Rev. Mod. Phys.* 72, 621 (2000).
- Useful links
  - xafs.org (especially see Tutorials section)
  - <http://www.i-x-s.org/> (International XAS society)
  - <http://www.csrrri.iit.edu/periodic-table.html> (absorption calculator)

## Further reading

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- Thickness effect: Stern and Kim, *Phys. Rev. B* 23, 3781 (1981).
- Particle size effect: Lu and Stern, *Nucl. Inst. Meth.* 212, 475 (1983).
- Glitches:
  - Bridges, Wang, Boyce, *Nucl. Instr. Meth. A* 307, 316 (1991); Bridges, Li, Wang, *Nucl. Instr. Meth. A* 320, 548 (1992); Li, Bridges, Wang, *Nucl. Instr. Meth. A* 340, 420 (1994).
- Number of independent data points: Stern, *Phys. Rev. B* 48, 9825 (1993).
- Theory vs. experiment:
  - Li, Bridges and Booth, *Phys. Rev. B* 52, 6332 (1995).
  - Kvítka, Bridges, van Dorssen, *Phys. Rev. B* 64, 214108 (2001).
- Polarized EXAFS:
  - Heald and Stern, *Phys. Rev. B* 16, 5549 (1977).
  - Booth and Bridges, *Physica Scripta* T115, 202 (2005). (Self-absorption)
- Hamilton (F-)test:
  - Hamilton, *Acta Cryst.* 18, 502 (1965).
  - Downward, Booth, Lukens and Bridges, *AIP Conf. Proc.* 882, 129 (2007). [http://lise.lbl.gov/chbooth/papers/Hamilton\\_XAFS13.pdf](http://lise.lbl.gov/chbooth/papers/Hamilton_XAFS13.pdf)